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WS₂ Nanotubes, 2D Nanomeshes, and 2D In-Plane Films Through One Single Chemical Vapor Deposition Route

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ABSTRACT: We demonstrate a versatile, catalyst free Chemical Vapor Deposition (CVD) process on insulating substrates capable of producing in one single stream one dimensional (1D) WO_{3-x} suboxides leading to a wide range of substrate-supported 2H-WS₂ polymorphs: a *tunable class* of out-of-plane (of the substrate) nanophases, with 1D nanotubes and a pure WS₂, two dimensional (2D) nanomesh (defined as a network of webbed, micron-size, few-layer 2D sheets) at its extremes; and in-plane (parallel to the substrate) mono- and few-layer 2D domains. This

entails a two-stage approach in which the $2\text{WO}_3 + 7\text{S} \rightarrow 2\text{WS}_2 + 3\text{SO}_2$ reaction is intentionally decoupled: first, various morphologies of nanowires or nanorods of high stoichiometry, $\text{WO}_{2.92}/\text{WO}_{2.9}$ suboxides (belonging to the class of Magnéli's phases) were formed, followed by their sulfurization to undergo reduction to the aforementioned WS_2 polymorphs. The continuous transition of WS_2 from nanotubes to the out-of-plane 2D nanomesh, *via* intermediary, mixed 1D-2D phases, delivers *tunable* functional properties; *e.g.* linear and non-linear optical properties, such as reflectivity (linked to optical excitations in the material), and second harmonic generation (SHG) and onset of saturable absorption. The SHG effect is very strong across the entire tunable class of WS_2 nanomaterials, weakest in nanotubes, and strongest in the 2D nanomesh. Furthermore, a mechanism *via* suboxide (WO_{3-x}) intermediate as a possible path to 2D domain growth is demonstrated. 2D, in-plane WS_2 domains grow *via* “*self-seeding and feeding*” where short $\text{WO}_{2.92}/\text{WO}_{2.9}$ nanorods provide both the nucleation sites and the precursor feed-stock. Understanding the reaction path (here, in the W-O-S space) is an emerging approach towards controlling the nucleation, growth and morphology of 2D domains and films of transition metal dichalcogenides (TMDs).

KEYWORDS: WS_2 and WO_{3-x} suboxides, transition metal dichalcogenides, two-dimensional layered materials, nanotubes, chemical vapor deposition (CVD) growth, linear and non-linear optical properties, second harmonic generation

Two-dimensional (2D) transition metal dichalcogenides (TMDs), the inorganic analogues of graphene, have attracted significant attention in recent years.¹⁻⁵ Chemical vapor deposition (CVD) has emerged as one of the most efficient and versatile methods for the large area synthesis of a

wide range of 2D TMDs.⁶⁻¹¹ By varying deposition parameters and improving the CVD apparatus, larger and larger domain TMD mono- and few-layer films have been recently reported.^{12,13}

Among the more than forty varieties of TMDs,¹⁴ WS₂ and WSe₂ have attracted significant attention due to their giant spin-orbit splitting, a property of particular interest for spintronics,¹⁵ as well as optical materials.^{16,17} In the case of WS₂, WO₃ and S powders are the precursors most widely used for growth by CVD.¹⁸ WO₃ is converted into WS₂ by sulfurization with the proposed reaction being $2\text{WO}_3 + 7\text{S} \rightarrow 2\text{WS}_2 + 3\text{SO}_2$.¹⁹ However, this conversion process is not trivial, as the W-atom sites in the WO₃ monoclinic cell differ significantly from those in the WS₂ hexagonal unit cell, requiring the nearest W-W inter-atomic distances along the *a* and *c* axes to change significantly, *i.e.* from 0.38 nm in WO₃ to 0.315 nm in WS₂ along the *a* axis, and from 0.38 nm in WO₃ to 0.62 nm in WS₂ along the *c* axis.²⁰ An intermediate WO_{3-x} suboxide stage, which would allow for partial displacement of W atoms and facilitate the conversion was demonstrated in the growth of WS₂ nanotubes,^{21,22} but has never been exploited so far for 2D growth. In general, in conventional in-plane (parallel to substrate) 2D growth, where WO₃ is rapidly reduced and sulfurized in an optimal S atmosphere, a couple of studies have reported oxi-sulfides instead of suboxides as the reaction intermediates, though no common growth mechanism has emerged.^{9,23}

In conventional 2D growth *via* CVD, the operational window for optimal, monolayer growth is very narrow. In general, it is necessary to avoid premature mixing of the WO₃ with S vapor as this interferes with WO₃ sublimation, causing a deficit of W precursor and, hence, precluding WS₂ formation on the growth substrate.²⁴ If S is introduced too late, however, an excess of WO₃ precursor will arrive at the substrate resulting in the growth of thick multi-layer WS₂ or W-nanowires.^{24,25} The question is then: how early (late) is too early (late)? Hu *et al.*²⁵ reported that introducing S six minutes before the WO₃ precursor reaches the target temperature provides

optimal conditions for maximum size growth of WS₂ (with $\sim 150\ \mu\text{m}$ lateral size of domains). However, if S was introduced only four minutes before the WO₃ precursor reaches the target temperature, the WS₂ domains became thicker and much smaller (20-30 μm in lateral size).²⁵ In contrast, in most of the reported works for CVD growth of WS₂, S was introduced simultaneously with WO₃:²⁶⁻³⁴ this corresponds to the case of “too late” in references.^{24,25} It is clear that the conditions for optimal CVD growth of monolayer WS₂ are very sensitive to the specific CVD configuration. It is thus of interest to explore if other 2D growth regimes exist that rely less on the precise timing of S and WO₃ introduction into the gas phase.

Here, we intentionally created an initial S-deficient environment, in order to decouple the overall CVD reaction into a two-stage process. We thus took the decoupling idea to the extreme and created a WO_{3-x} phase and nanorod morphologies as precursors, which we then sulfurized. This approach has similarities with the concept underpinning the synthesis of WS₂ nanotubes, obtained by sulfurization of WO_{3-x} nanowires.^{35,36} As a result of stage decoupling, which does not occur in conventional CVD of 2D TMDs, we were able to show that 2D growth of WS₂ can occur *via* the WO_{2.92}/WO_{2.9} suboxides, and hence demonstrate a viable suboxide path to 2D growth. This approach also allowed us to demonstrate a facile, tunable CVD route capable of flexibly producing *in a single process stream* a variety of WS₂ phases, spanning from 1D to 2D, as well as grown in-plane or out-of-plane. Through this process, a 2D nanomesh, described as an out-of-plane network of webbed 2D sheets (of mainly one to three WS₂ layers) with large, μm -range lateral domain size was created; this is the ultimate stage in an evolutionary process started with the WO_{2.92}/WO_{2.9} nanowires, from which WS₂ nanotubes with WO_{3-x} cores formed, which then gave rise to 2D sheets as the S-mediated reduction process progressed. The tunability and functionality of this class of WS₂ materials is demonstrated through comparative investigations of the optical properties of

representative phases obtained at progressing stages: the 1D, nanotube-based phase, vs an intermediary phase of mixed 1D/2D content, and finally, vs the 2D nanomesh. We thus measured (i) reflectivity and correlated it with optical excitations, as well as (ii) non-linear optical properties, *i.e.* second harmonic generation (SHG) and onset of saturable absorption, in the three types of materials. All the WS₂ materials in the class showed strong non-linear optical properties, with the 2D nanomesh being most SHG-active. Finally, we showed that in this decoupled, two-stage growth, in-plane 2D mono- and few-layer WS₂ can be grown in a “*self-seeding and feeding*” process, where the nucleation sites and the source of precursor material are provided by the same phase; unlike in heterogeneous seeding processes demonstrated so far, where organic molecular species were used as seeds.^{6,8,37}

Results and discussion

Figure 1 presents the flow chart for the catalyst-free CVD processes discussed in this work, showing the inter-relation, and contrasting differences, between the conventional growth of 2D domains³⁸ and the processes and phases enabled by the decoupling of the overall reaction into two distinct stages.

During 2D growth the reaction ideally happens in the vapor phase: WO₃ is partially reduced by the sulfur vapor to form volatile WO_{3-x} suboxide species, which are then further sulfurized to form large crystalline domains of mono- and few-layer WS₂ on substrates. However, the reaction occurs too fast for any intermediary stages to be observed and confirmed. In contrast, here we intentionally decouple the reaction into two stages. In our decoupled reaction, we engineered a first reaction stage (WO₃ partial reduction performed below atmospheric pressure, blue arrows on Figure 1) where the vapor phase is S-deficient, leading to the initial growth of one-dimensional

(1D) WO_{3-x} morphologies, such as nanowires or short nanorods. Then, in a second stage (sulfurization at atmospheric pressure, red arrows on Figure 1), the nanowires/nanorods are reacted in an S-rich atmosphere for varying amounts of time, ultimately leading to the formation of pure WS_2 nanophases characterized by the emergence of 2D domains and crystallites. It is apparent (see Figures 2-5) that the type of 1D suboxide morphology in the first stage and the period of sulfurization in the second stage control the resulting WS_2 nanophases: (i) using long, out-of-plane WO_{3-x} nanowires as precursors yielded WS_2 nanotubes, a hybrid 1D/2D film, or an out-of-plane 2D nanomesh, while (ii) short nanorod precursors yielded in-plane 2D WS_2 growth. By performing further structural analysis, we were able to demonstrate that the two growth stages map onto the two hypothesized reaction stages:^{39,40} (1) $2\text{WO}_3 + x\text{S} \rightarrow 2\text{WO}_{3-x} + x\text{SO}_2$, and (2) $2\text{WO}_{3-x} + (7-x)\text{S} \rightarrow 2\text{WS}_2 + (3-x)\text{SO}_2$. We thus confirm this two-stage reaction mechanism, and the involvement of suboxides as intermediary sub-species.

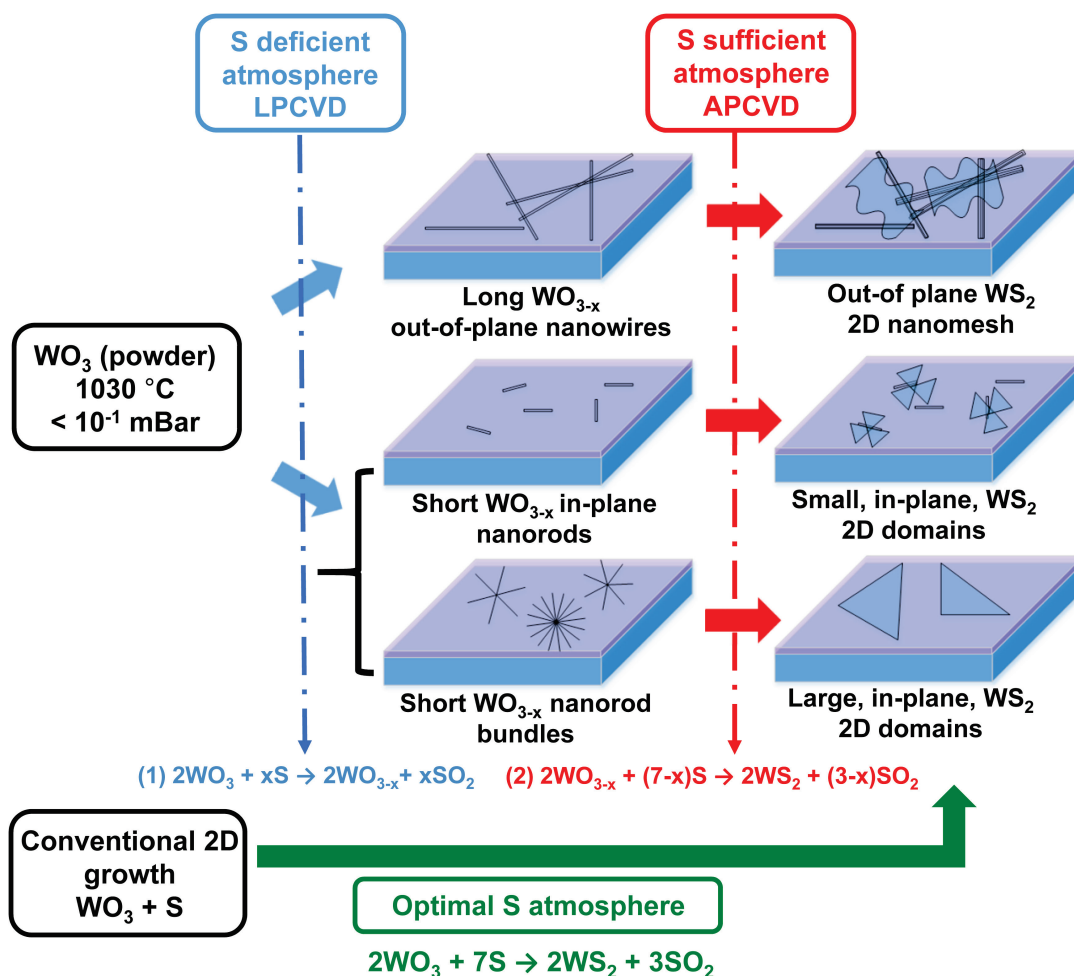


Figure 1. Flow-chart describing the decoupled, two stage strategy for synthesis of crystalline WS₂ nanophases starting from WO₃ and sulfur powders as precursors, mapped onto a two-stage reaction. Stage 1 (blue arrows), a low-pressure CVD (LPCVD) process, where partial reduction of WO₃ takes place in an S deficient atmosphere, leads to the formation of various WO_{3-x} morphologies, *i.e.* long out-of-plane nanowires, short in-plane nanorods, and short nanorod bundles. From each of these morphologies, distinct, pure WS₂ nanophases result after sulfurization in stage 2 (red arrows), such as an out-of-plane 2D nanomesh, as well as 2D in-plane domains of various sizes; this is an atmospheric pressure CVD (APCVD) process. Conventional in-plane 2D domain growth, obtained by WO₃ fast reduction in an optimal S atmosphere, is indicated by the green arrow.

WO_{3-x} nanowire/nanorod morphologies were obtained in the first reaction stage (Figure 1), using a home-built low-pressure CVD (LPCVD) reactor involving a horizontal furnace with a temperature gradient (Methods and Supporting Information, Figure S1). The boat containing the WO₃ precursor was placed in the center of the furnace, within its constant temperature zone; temperature was ramped to 1030 °C, at a pressure below 10⁻¹ mBar, and then held constant for 20 minutes, to ensure sufficient sublimation. Subsequently, the sulfur powder, placed in a boat 40 cm upstream of the WO₃ boat, was heated to 200 °C over 10 minutes, and then co-evaporated together with the WO₃ over 15 minutes. Another boat with four pockets, each 2 cm long, and containing SiO₂/Si substrates, was placed 6 cm downstream of the WO₃ boat, in a zone with a temperature gradient. Only argon was used for transporting the WO₃ and sulfur vapor to the SiO₂/Si substrates. According to the temperature profile of the furnace, there is a temperature drop of about 60 °C between each substrate-containing pocket. This enabled a W precursor concentration gradient across the various substrate locations,^{41,42} leading to a continuous variation in the growth conditions. In contrast, the long separation distance between the S and substrate boats ensured that the S vapor concentration gradient across the Si/SiO₂ substrates can be ignored, unlike that of WO₃.

Depending on the position and temperature of the substrate relative to the W precursor, different WO_{3-x} morphologies were obtained (Figures 2 and 5, see also Supporting Information, Figure S1).

(i) In the pocket furthest from the W precursor, the relatively low temperature of around 780 °C, induces a low diffusion rate of the precursor, leading to the precursor being trapped at many random sites on the substrate. After the nucleation sites become saturated with precursor, further trapping of precursor results in crystallization and growth. A high carrier gas flow rate (~150 sccm) promotes mass transfer, which contributes to a fast crystal growth rate⁴¹ leading to the formation

of *long, out-of-plane nanowires* (Figures 2(a) and 3(a), and Supporting Information, Figure S2). (ii) The pocket closer to the WO_3 boat was reached by a higher concentration of W precursor, while also being held at the highest temperature, 1000 °C, of all the substrates. In general, a high temperature induces a high diffusion rate of the precursor, favoring film growth. On the other hand, too high a temperature causes large thermal turbulence, resulting in an instability of as-grown nucleation sites⁴³ and hindering growth. Hence, under these conditions of temperature and W precursor concentration *short nanorod bundles* were formed (Figure 5(d), and Supporting Information, Figure S2). (iii) In between these high and low temperature regimes, in a pocket located in an intermediate position at about 960 °C, the decrease in precursor concentration results in a crystal growth rate slow-down: the positive influence of a high flow rate balanced by a moderate diffusion rate of precursor at a moderate temperature leads to stable, while slow, crystal growth under thermodynamic control. Hence, *short, in-plane nanorods* could be grown (Figure 5(b)).

We now analyze the outcome of stage 2 – sulfurization – of the decoupled reaction diagrammatically shown in Figure 1, where each of the three nanowire/nanorod morphologies described above are reacted with sulfur.

WO_{3-x} long nanowires as precursors. Figure 2(a) shows the WO_{3-x} nanowires grown on the SiO_2/Si substrate (Methods): their diameters fall in a narrow range, 10 to 30 nm, and they can reach several microns in length. A combination of X-ray diffraction (XRD) (Supporting Information, Figure S2) and high-resolution transmission electron microscopy (HRTEM) showed that $\text{WO}_{2.92}$ ($\text{W}_{25}\text{O}_{73}$) and $\text{WO}_{2.9}$ ($\text{W}_{20}\text{O}_{58}$) are the phases encountered in the nanowires (Supporting Information, Figure S2 (a-d)). Indeed, Fast Fourier Transform (FFT) analysis of the examples given in Figures S2 (c-d) show periodicities along the long axis of the nanorods that correspond to

3.82 Å and 3.78 Å, respectively, which are in good agreement with the *b* lattice parameters of monoclinic WO_{2.92}⁴⁴ and WO_{2.9}.⁴⁵ Both these suboxides belong to the sub-stoichiometric Magnéli's phases, which have the series formula of W_nO_{3n-2}.⁴⁶ Most importantly, both suboxides are non-volatile (see Methods) but can be reduced further into volatile suboxides (see discussion below) at the temperatures used in the subsequent sulfurization stage from Figure 1; this is consequential, as it strongly influences the type of WS₂ nanostructures that can be obtained by sulfurization, as demonstrated in the following.

The as-grown WO_{2.92}/WO_{2.9} nanowires on SiO₂/Si were sulfurized as described in Methods, at atmospheric pressure (an APCVD process), in the first instance over ~ 10 minutes. Figure 2(b) shows a scanning electron microscopy (SEM) image of the resulting post-sulfurized nanowires: two types of material, with different electronic contrast, can be observed. The brighter areas have very broad Raman peaks at 271, 326, 714 and 803 cm⁻¹ (Figure 2(d)). Peaks centered at 714 and 803 cm⁻¹ are attributed to W-O stretching vibration modes, while the two lower peaks at 272 and 326 cm⁻¹ are induced by O-W-O bending vibration modes,⁴⁷ identifying these regions as non-converted, pure suboxide phases. Raman spectroscopy confirms that the regions that appear dark in both optical and SEM images are 2H-WS₂ (Figure 2(c), and Supporting Information, Figure S3): the 352.5 and 418 cm⁻¹ peaks correspond to the E_{2g}¹ and A_{1g} vibrational modes, respectively, of this phase, while their spectral distance of ~ 65.5 cm⁻¹ shows that the phase is made up of few-layer WS₂ nanotubes.⁴⁸ HRTEM (Figures 2(e-f)) confirms that the sulfurized nanowire-shaped morphologies are actually the suboxide nanowires transforming into multi-layered WS₂ nanotubes. The HRTEM images and their associated FFTs (inset panels) give a spacing between the layers of the nanotubes of about 0.62 nm, consistent with the (002) d-spacing within a multilayer 2H-WS₂ crystal. The nanotubes are partially filled with WO_{2.92} or WO_{2.9} suboxides cores, as demonstrated

by Figure 2(f); the associated FFT identifies the core inside the nanotube as $\text{WO}_{2.92}$ based on its b lattice parameter. However, despite the presence of W suboxide cores inside some of the nanotubes, Raman spectroscopy does not detect any of their W-O vibration modes; a similar behavior was previously reported for other core-shell systems.^{48,49} The coexistence of WS_2 nanotubes and W suboxides is reminiscent, in this respect, of the work from Tenne's group on the synthesis of MoS_2 and WS_2 nanotubes.^{36,50} Therefore, it is reasonable to assume that the WS_2 -rich areas from Figure 2(b) are actually a proto-stage of the growth of WS_2 nanotubes around the suboxide nanowire cores.

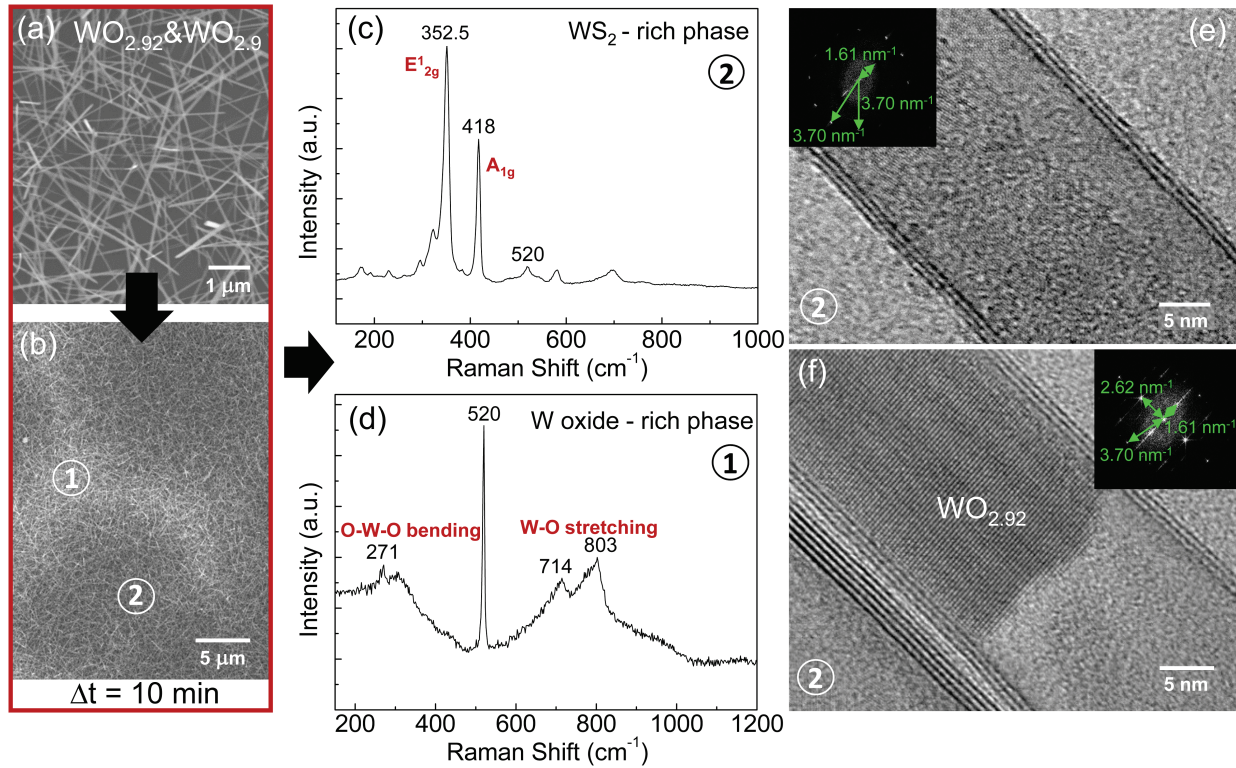


Figure 2. Long, out-of-plane nanowires of $\text{WO}_{2.92}$ and $\text{WO}_{2.9}$ suboxide, Magnéli phases leading to the formation of few-layer multi-walled nanotubes with suboxide cores. (a-b) SEM of pure WO_{3-x} nanowires before and after 10 minutes of sulfurization, respectively. The example in (b) shows a predominant WS_2 -rich phase (labelled “2”), interspersed with a residual pure WO_{3-x} phase (labelled “1”). Their respective Raman spectra (excitation wavelength of 532 nm) are shown in (c)

and (d). (e-f) TEM images of the sulfurized nanorods showing multi-walled nanotubes of large diameter and relatively few layers. In (e), the highlighted FFT inset vectors correspond to 0.27 nm, the distance between the (100) planes of 2H-WS₂ crystals, and to 0.62 nm, the van der Waals inter-tube distance. In (f), the WO_{2.92} suboxide core nanowire is still visible. The FFT inset highlights, in addition to the distances identified in (e), 0.382 nm along the long axis of the suboxide core, which corresponds to the distance between the (010) planes of monoclinic WO_{2.92}.

In contrast to here, previous works on the synthesis of WS₂ nanotubes mainly used W oxide nanowires formed by the hydrothermal method, which primarily consisted of the non-volatile, low-stoichiometry WO_{2.72} (W₁₈O₄₉) phase: this is the so-called reduction-resistance phase, and will not undergo further reduction.^{36,51} In their work based on vapor phase reaction in a fluidized bed reactor, Tenne *et al.*³⁵ have found that several intermediate, higher stoichiometry suboxides could also be present during the formation of their WO_{3-x} nanowires; however, the non-volatile WO_{2.72} was identified as the resulting stable phase in the nanowires, which then served as a template for the subsequent sulfurization reaction yielding WS₂ nanotubes. The transformation of the suboxide nanowires into WS₂ nanotubes is then diffusion-controlled, and such conversion takes place slowly and layer-by-layer relying on the sulfur diffusing to the core. In our case, however, with further annealing in a S-rich environment the high stoichiometry WO_{2.92} or WO_{2.9} nanowire cores, rather than being sulfurized layer-by-layer, are able to transform to lower stoichiometry, volatile WO_{3-x} phases; 3-x could be 2.89 (*i.e.* WO_{2.89} (W₁₉O₅₅))⁵² or in the range 2.72 – 2.83 that contains volatile phases.^{36,51,52} Such phases can then escape through the open/defective ends of the nanotubes. This results in a higher conversion rate to WS₂, which can then nucleate and grow as 2D sheets outside the nanotubes (see Figure 4 and related discussion).

Hence, sulfurization, in the first stage, produces single- or few-wall WS₂ nanotubes, with partial cores of suboxide still present; the layer-by-layer conversion does not continue long enough to involve full transformation of the WO_{2.92}/WO_{2.9} cores into the nanotube phase as suboxide material leaves the nanotubes. In contrast, from the non-volatile WO_{2.72} phase thick multi-layered nanotubes with empty cores are generated. For instance, as shown by HRTEM in Figures 2 (e-f), we could obtain tri-layer WS₂ nanotubes of diameter more than 25 nm using the WO_{2.92}/WO_{2.9} precursors; while from the lower stoichiometry, reduction-resistant, WO_{2.72} precursor, nanotubes of around 20 nm in diameter have more than 10 layers.⁵³

In order to determine the ultimate effect of the sulfurization, the long, out-of-plane nanowires were continuously sulfurized under the same conditions for a large period, typically less than three hours. A final morphology was then achieved: Figure 3(b) shows a two-dimensional (2D) nanomesh structure of webbed 2D crystallites, extending out-of-plane for microns (up to ~ 10 μm), and with a very large specific surface area. Figure 3(c) presents the TEM image, and associated FFT, of a typical crystallite: this has a hexagonal lattice structure with 0.27 nm periodicity resulting from the (100) planes of 2H-WS₂,⁵⁴ and two layers are visible. A representative nanomesh XRD spectrum is shown in Figure 3(d): all the diffraction peaks are indexed relative to the hexagonal P63/mmc space group, indicating that the structure of the WS₂ phase is 2H-WS₂, while there is almost no trace of W suboxide peaks. The sharpness of the peaks demonstrates the good crystallinity of the sample overall.

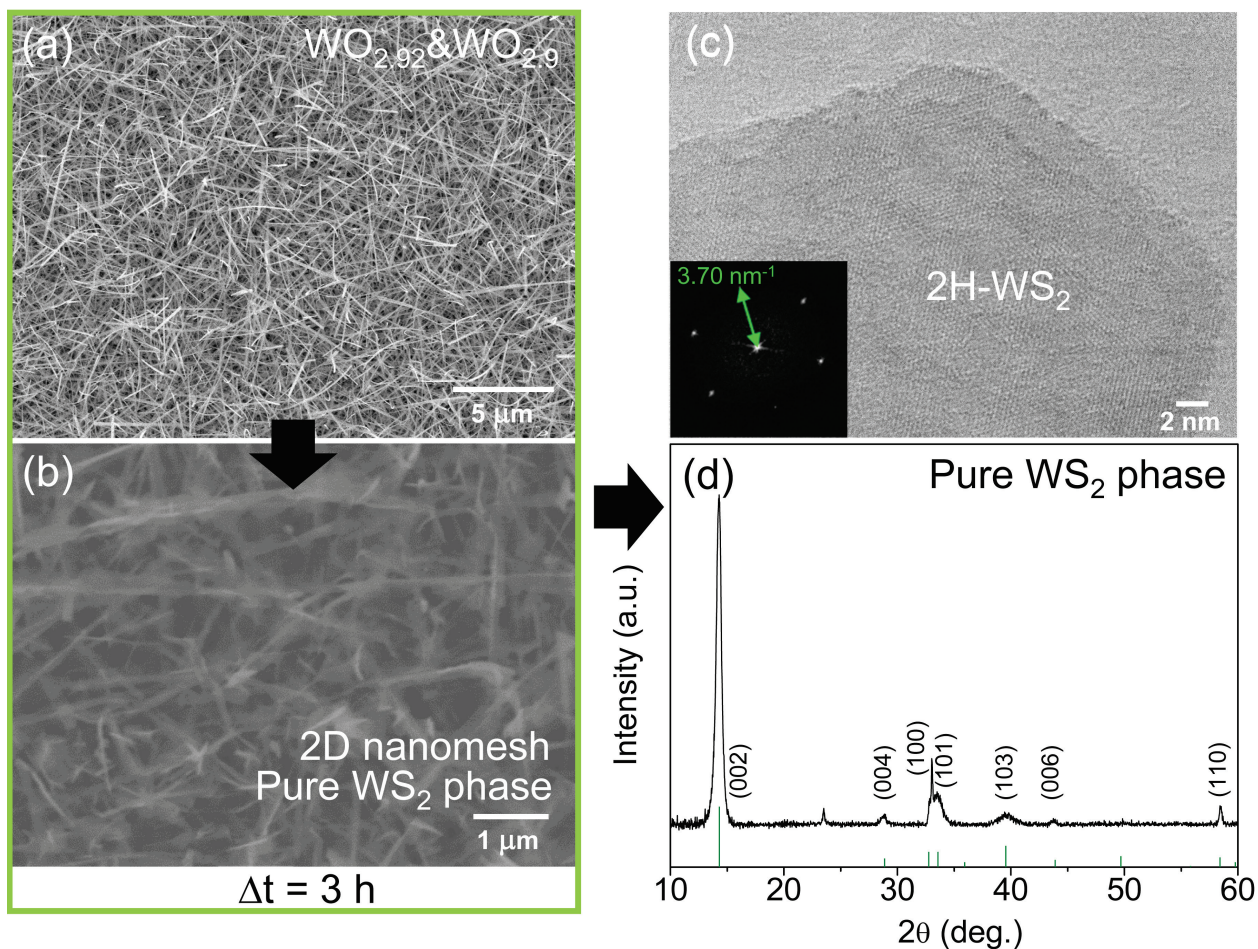


Figure 3. Full sulfurization of long, out-of-plane $\text{WO}_{2.92}$ and $\text{WO}_{2.9}$ suboxide nanowires, shown in (a), leads to a pure WS_2 2D nanomesh, shown in (b). The sulfurization was typically performed over a period Δt of 3 hours. The emergence and purity of the 2H- WS_2 phase was verified by a combination of (c) HRTEM (and associated FFT, example shown in inset), and (d) XRD, where the identified crystallographic planes are also shown. In (c), a typical WS_2 crystallite with 2 layers is shown.

Between these two extremes, the WS_2 material can be evolved in a continuous manner, with a variable proportion of nanotube (1D) and 2D phases, as depicted by stages (i-v) on Figure 4(a). Figures 4 (b-e) shows TEM images of the material at different stages of sulfurization: after the formation of an initial nanotube sheath around the $\text{WO}_{2.92}/\text{WO}_{2.9}$ cores, volatile WO_{3-x} suboxide

(obtained by subsequent reduction of the non-volatile $\text{WO}_{2.92}/\text{WO}_{2.9}$) forms and then leaves the nanotubes through their open ends (or, alternatively, through wall defects that sometimes develop) (Figure 4(b)), and nucleates 2D crystallites at the nanotubes' ends (Figure 4(c)). The nanotube exterior provides an ideal surface for subsequent epitaxial growth of 2D domains, the evolution of which is often accompanied by a gradual opening of the nanotubes, presumably catalyzed by stresses on the nanotube bonds induced by the 2D growth (Figures 4(d-e)). “Un-zipping” of WS_2 nanotubes was previously reported, though based on Li intercalation.⁵⁵ Once opened, the 2D sheets and the nanotube edge can also fuse, as shown in the inset of Figure 4(d). Figure 4(a) shows diagrammatically the various stages of this evolution, from $\text{WO}_{2.92}/\text{WO}_{2.9}$ nanowires, through WS_2 nanotubes (with partial suboxide cores), then hybrid 1D/2D materials, and finally into a pure WS_2 2D nanomesh.

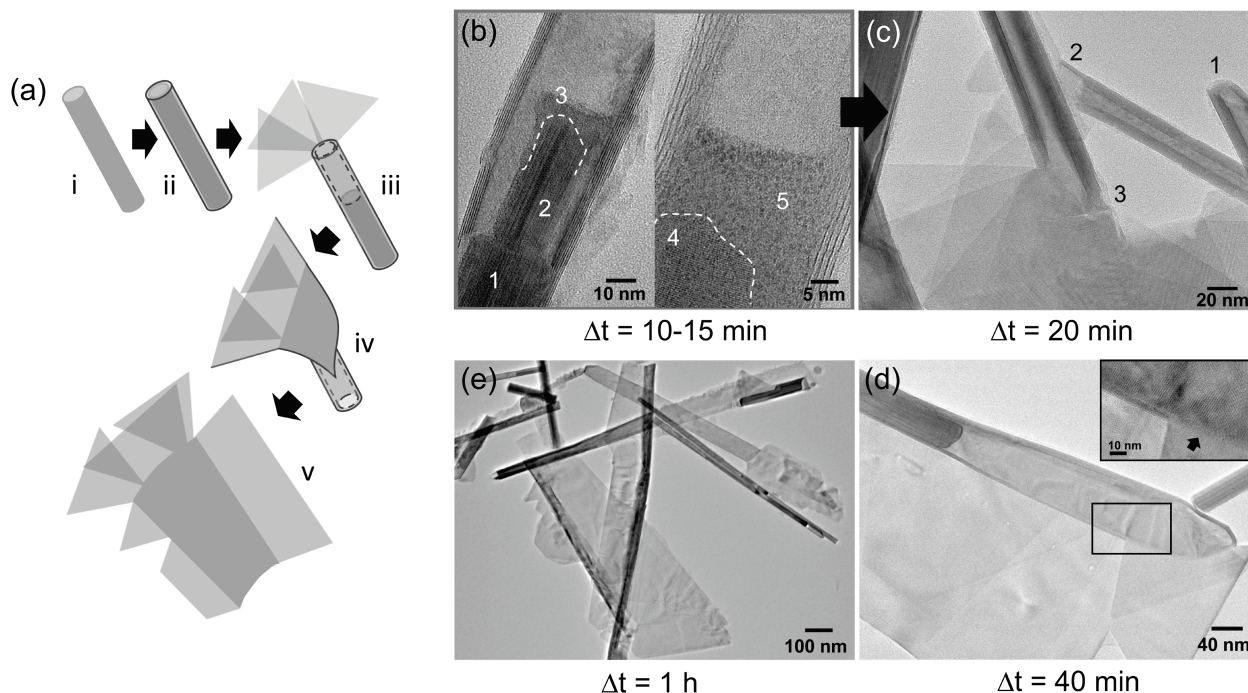


Figure 4. Evolution with sulfurization time, Δt , of the suboxide cores into WS_2 nanophases. (a) Several stages (i-v) were identified, mapping onto representative TEM images (c-e): $\text{WO}_{2.92}/\text{WO}_{2.9}$

nanowires (i) become covered with few-layer nanotube sheaths (ii) in a layer-by-layer conversion of suboxide into 2H-WS₂, (iii) WO_{2.92}/WO_{2.9} core suboxide reduces to a lower stoichiometry, volatile suboxide which leaves the tubes and nucleates into 2H-WS₂ sheets at the tube apex, (iv) WS₂ 2D domains grow by epitaxy on the body of the nanotubes, which are then subjected to gradual opening, (v) finally, nanotubes fully open and merge with extended 2D 2H-WS₂ sheets. (b) The emergence of the volatile suboxide phase, with 1, 2 and 4 showing crystalline suboxide, while 3 and 5 showing regions of reduced crystallinity (boundary between the two regions shown with dashed line). (c) WS₂ nanotubes (2 and 3) with no suboxide filling and nucleated 2H-WS₂ sheets at the apex of the tube, while (1) shows the breached end of a nanotube through which filling material can escape. (d) Large 2D WS₂ sheets nucleated all along the body of the nanotube, which is still partially filled. The unfilled region shows gradual nanotube opening, while the zoomed area highlighted in the inset figure shows the nanotube layers fusing with the grown 2D sheets. (e) Extended, micron-wide 2D sheets grown all along the nanotubes' bodies.

The formation of the pure WS₂ 2D nanomesh, with extensive 2D content (Figure 3(b)) is in contrast to other recently reported hybrid phases which were a mixture of 2D WS₂ crystallites and WO₃,⁵⁶ or had a mixed 1D-2D character, with a main nanowire phase and a small 2D phase content.⁵⁷ Temperature-dependent conductivity measurements on our pure WS₂ 2D nanomesh (Supporting Information, Figure S5) demonstrate the semiconducting nature of this phase, while an activation energy $E_a \approx 0.33$ eV indicates thermally activated transport, *via* a defect band, around (and just below) room temperature. Further optical properties of this nanomesh are presented in the last section.

WO_{3-x} short nanorods as precursors. Figure 5(a) shows the results of atmospheric pressure sulfurization in a region of lower density of suboxide nanowires. It is clear that less dense nanowires yield relatively larger and more separated, out-of-plane 2D WS₂ crystallites. This suggests that if the W suboxide nanowires are well-separated and oriented in plane they may be used as seeds for the growth of in-plane 2D WS₂ films.

Hence, as-grown in-plane, single, short WO_{2.92}/WO_{2.9} nanorods on SiO₂/Si were similarly sulfurized (Methods) and Figures 5(b-c) show the result of such a scenario: in-plane, triangular, few-layer 2D domains grow from the nanorods at their basis. This root growth is enabled by the same transformation stage sequence shown in Figure 4(a), with the volatile suboxide emerging from the WS₂ nanotubes and converting to WS₂ domains that nucleate directly onto the SiO₂/Si substrate, thus keeping the material localized around the original nanorod. Raman spectroscopy confirms that the domains grown are WS₂, albeit thicker than monolayers (Figure 5(f) and Supporting Information, Figure S5(b)). This result demonstrates the feasibility of using W suboxide nanorods as *seeds* for the 2D in-plane growth of WS₂. Seeded growth of 2D WS₂ domains has been studied by using either large aromatic molecules (*e.g.* perylene-3,4,9,10-tetracarboxylic acid tetra-potassium salt (PTAS))^{6,8,37} or patterned oxide precursor particles⁵⁸ as externally introduced nucleation sites, over which W- and S-carrying species were subsequently introduced. However, in our case, the seed is provided by the suboxide nanorods without introducing other external contamination. Moreover, the 2D domain growth can be treated as a “*self-seeding and feeding*” one, in which the suboxide nanorods provide both the nucleation sites and the W precursor feed-stock for the growth of layers.

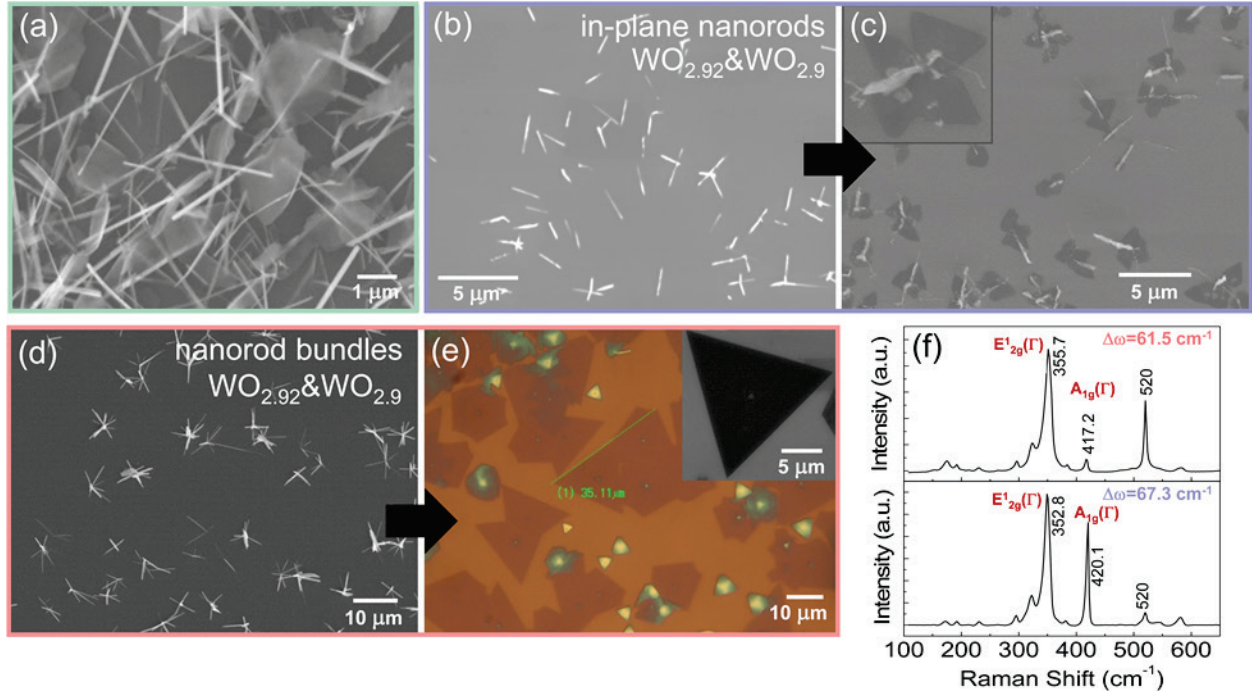


Figure 5. Effect of sulfurization of sparse $\text{WO}_{2.92}/\text{WO}_{2.9}$ nanorods revealing seeded growth of in-plane 2D 2H- WS_2 domains. (a) Sulfurization of low density out-of-plane nanowires leads to extended and more separated WS_2 2D crystallites; shown by SEM. (b-c) In-plane, individual, short nanorods lead to seeded, root-growth of polygonal domains of multi-layered WS_2 ; shown by SEM. (d-e) Bundles of short nanorods lead to seeded, in-plane growth of larger single-layered 2D WS_2 domains: (e) is a bright field, optical image, while (d) and inset of (e) are SEM images. (f) Raman spectroscopy (at 532 nm excitation) of single-layered WS_2 from (e), in top panel; and of multi-layered WS_2 from (c), in bottom panel. The spectral distance $\Delta\omega$ between the $E'_{2g}(\Gamma)$ and $A_{1g}(\Gamma)$ vibrational modes of WS_2 is used to identify the number of layers within the 2D domains.

In “self-seeding and feeding”, the size of the in-plane 2D domains that can be grown is constrained by the amount of W precursor available in the seeds. Hence, larger 2D domains could be grown by increasing the amount of precursor delivered by the nanorod seeds. Therefore, as shown in Figure 5(d), we used clusters of short W suboxide nanorods as the precursors in the

sulfurization stage; these clusters have also been confirmed by XRD to be a mixture of $\text{WO}_{2.92}$ and $\text{WO}_{2.9}$ phases (Supporting Information, Figure S2). Optical/SEM images (Figure 5(e)) and Raman characterization (Figure 5(f) and Supporting Information, Figure S5(a)) show that their sulfurization resulted in the growth of in-plane triangular domains of predominantly mono-layer 2D WS_2 domains; these domains are also substantially larger than the multi-layer domains shown in Figure 5(c) obtained from single nanorods as seeds. As the amount of precursor and distance to the substrate increased compared to the case of single, in-plane nanorods, the WS_2 domains now grow *via* a mixture of reaction mechanisms: root growth (as observed in Figure 5(c)) competes with gas phase transport and reaction. Indeed, by the reduction of $\text{WO}_{2.92}/\text{WO}_{2.9}$ to lower-stoichiometry, volatile WO_{3-x} phases (as *per* the mechanism depicted in Figure 4(a)), the latter can readily transfer to vapor phase as *in-situ* precursor to supply the conversion reaction. The W suboxide seed growth demonstrated above is distinct from a recently shown process where WS_2 nanotubes were sublimated in order to induce WS_2 monolayer growth by vapor phase transport and surface diffusion.^{59,60}

“Self-seeding and feeding” from precursor nanowires could potentially be harnessed by controlling nanowire growth *via* substrate engineering, thereby allowing for the positional control of WS_2 domain growth; while the limited feed-stock of material would limit the resulting domain size and facilitate patterning. For example, when sapphire, a substrate frequently used in TMD growth,^{19,61-63} with unstable orientations is annealed at high temperature, it spontaneously becomes periodically faceted.⁶⁴ Specifically, the mis-cut C plane (0001) (2° toward $[1\bar{1}00]$) facets into L-shaped nanosteps; while the M plane ($10\bar{1}0$) facets into V-shaped nanogrooves. It has been demonstrated that various types of nanowires (*e.g.* of ZnO ,⁶⁵ GaAs ,⁶⁶ or GaN ⁶⁷) *etc.*) could be

grown with a good degree of alignment on both these facets. Furthermore, tungsten oxide nanorods have been reported to epitaxially grow on mica using a simple vapor–solid growth process.⁶⁸

Figure 6 shows as a corollary the various pathways uncovered so far in previous works for the 2D growth of TMDs from transition metal tri-oxides.^{9,23,69,70} On paths 2 and 3, corresponding to conventional 2D growth, W or Mo oxi-sulfide nanoparticles first formed and were adsorbed on substrates as nucleation cores for further reduction. No common growth mechanism has emerged from these studies, the various proposed scenarios being inconsistent with each other and resulting in different and complex reactions paths. In contrast, path 1 highlights the suboxide route to 2D growth demonstrated in this work. A common mechanism can explain both in-plane and out-of-plane 2D growth processes: these rely on the initial formation of $\text{WO}_{2.92}$ and $\text{WO}_{2.9}$ (blue arrow on the W-O-S phase diagram), Our process of 2D WS_2 synthesis always starts with the formation of few-layer WS_2 nanotubes around the $\text{WO}_{2.92}/\text{WO}_{2.92}$ cores. Nanotube formation is controlled by the specific crystallographic structure of the Magnéli suboxide phases which contain crystallographic shear (CS) planes (Supporting Information, Figure S6) created as result of oxygen vacancies introduced by reduction. At atomic level, the shear process is equivalent to the diffusion of an atom to a neighboring lattice vacancy; however it was previously proposed that the octahedra hop as a whole during the process leading to the formation of edge sharing octahedral units, *i.e.* the CS planes (Supporting Information, Figure S6), as opposed to corner sharing ones.^{20,71} While the reaction progresses, regions of such edge-sharing octahedral units develop across the crystal. The edge-sharing octahedral units in $\text{WO}_{2.92}$ and $\text{WO}_{2.9}$ are now similar to the 1T- WS_2 octahedral structure (Supporting Information, Figure S6). As the sulfurization proceeds, O atoms are released from the lattices of the Magnéli phases and replaced by S atoms, leading to the expansion of the unit cell along the c axis, while the W-W bond length in the edge-sharing octahedral units of

$\text{WO}_{2.92}/\text{WO}_{2.9}$ is already very similar to that of 2H- WS_2 (Supporting Information, Figure S6). This process is depicted by the dotted arrow on the W-O-S phase diagram of path 1 on Figure 6. This $\text{WO}_{2.92}/\text{WO}_{2.9}$ route is supported by recent findings that starting directly from $\text{WO}_{2.9}$ as a precursor (as opposed to WO_3 and without controlling the intermediary reaction) promotes 2D growth of larger and more uniform domains of WSe_2/WS_2 .^{27,72} Finally, in our scenario, the 2D WS_2 sheets always form after the formation of the nanotubes, and the reaction path is depicted by the green-red path on the W-O-S phase diagram: thus, the residual $\text{WO}_{2.92}/\text{WO}_{2.9}$ from inside the nanotubes converts into lower stoichiometry, volatile Magnéli WO_{3-x} phases, which can then escape the nanotubes and nucleate as WS_2 outside them, and then evolve into extended 2D sheets as described in Figure 4(a).

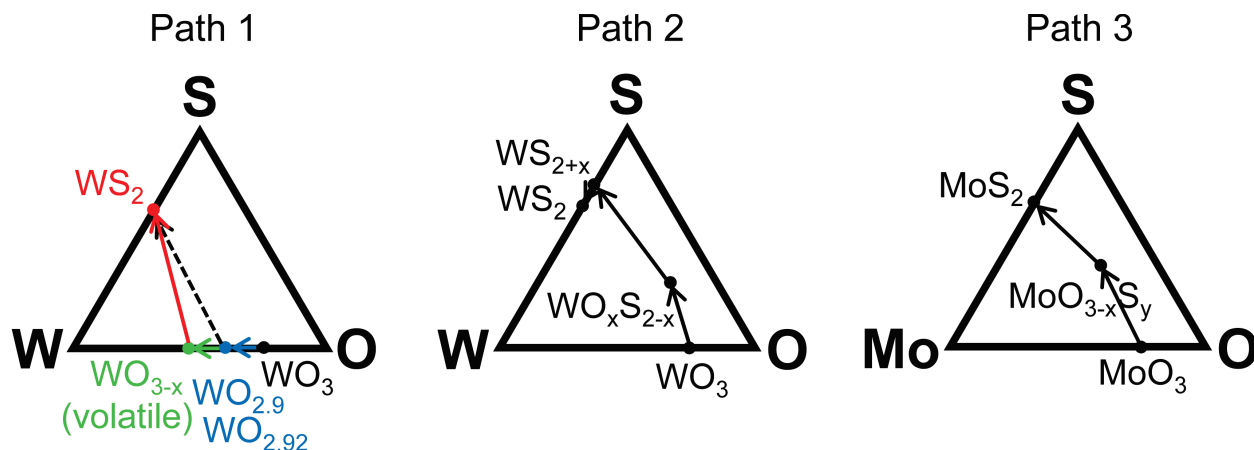


Figure 6. W–O–S ternary phase diagrams showing reaction pathways to 2D 2H- WS_2 during CVD growth from WO_3 and sulfur precursors. Path 1 (left diagram) describes a reaction mechanism *via* the non-volatile $\text{WO}_{2.92}/\text{WO}_{2.9}$ phases and their subsequent reduction to lower stoichiometry, volatile WO_{3-x} phases, as shown in this work. 2D growth corresponds to the blue-green-red path, while the black, dotted path corresponds to 1D (nanotube) phase synthesis. Paths 2 (middle) and 3 (right), identified in conventional 2D growth of WS_2 , highlight reaction mechanisms where oxisulfides are the intermediary compounds.

Finally, we investigated some of the opportunities afforded by the tunability of the relative 1D to 2D content of the material. Hence, we measured and contrasted the linear optical properties (Methods) of out-of-plane, nanotube-rich and 2D nanomesh samples, as well as an intermediary sample with mixed 1D/2D content, and related them to the relevant optical excitations that can occur in them. The non-linear optical behavior of these three samples was subsequently tested (Methods). Figure 7(a), left, shows a photograph of the 2D nanomesh sample, demonstrating its homogeneity over a large area ($> 8 \times 8 \text{ mm}^2$); while at a magnification $\times 100$, randomly distributed structures appear well resolved in dark-field illumination (Figure 7(a), right). In order to obtain reflectance spectra, illumination was switched to bright-field and measurements were taken at normal incidence with unpolarized light; Figure 7(b) shows characteristic optical reflection spectra from all three samples, (i) nanotube-rich, (ii) with intermediary 1D/2D content, and (iii) the 2D nanomesh, normalized to the reflectivity of the SiO_2/Si substrate. Over the 400 – 650 nm range, all three samples exhibit dips in reflectivity, marked with A, B, and C, corresponding to increased extinction; these can be attributed to excitonic resonances, for A and B, and optical absorption between density of states peaks in the valence and conduction bands for C, in agreement with previous reports.^{73,74} For the nanotube-rich sample, these spectral features are located at 628, 521.7, and around 450 nm, respectively, and red-shifted relative to the intermediary 1D/2D content sample, and the 2D nanomesh. The intermediary, mixed 1D/2D content sample has spectral features close to the 2D nanomesh, owing to its large 2D content, though its non-linear optical properties are distinctive compared to the other two samples in the series (see Figure 8(b)). For the 2D nanomesh, A, B and C are located at 622.5, 515.8 and ~ 443 nm, respectively, in good agreement with spectra of mechanically exfoliated mono- and bi-layer WS_2 sheets,⁷³ indicating the prevalence of mono- and bi-layer WS_2 sheets in our material; in comparison, thicker 2D sheets

have their spectral features red-shifted.⁷³ The broadening of the A, B, and C features relative to those measured on mechanically exfoliated WS₂ 2D layers of well-defined thickness⁷³ likely reflects the (thickness) polydisperse nature of all three samples, as well as the presence of defects in these materials. Above 700 nm, in the nanotube-rich sample there is a very broad spectral feature centered around 760 nm, and a counterpart can be seen around 840 nm in both the 2D nanomesh sample and the one with mixed 1D/2D content. Due to their broadness and the large spectral difference (~ 80 nm) between their location for the three samples, as well as the lack of known possible excitations in this spectral region in (perfect) laterally extended WS₂ sheets (mono- or few-layer) or bulk crystals, it is more likely that these spectral features are caused by geometrical/morphological characteristics of the two samples. For nanotubes of diameters comparable with the excitation light wavelength, and with many layers (*i.e.* creating a material with high refractive index), cavity mode resonances can be excited: for example, 760 nm excitation can excite cavity modes in a 70 nm radius WS₂ multi-layer nanotube, while by decreasing the nanotube radius the wavelength of the light that can excite cavity modes decreases.⁷⁴ Consequently, as the nanotube diameters in our nanotube-rich sample are in the 10 to 30 nm range, no cavity resonances can be excited in the spectral range investigated here, and such excitations can thereby be ruled out. Most likely, the broad spectral features are sample geometry- or morphology-related, for example the result of a collective behavior of the material. Tentatively, we propose an explanation based on the nanotube-rich material and the 2D nanomesh being approximated as homogenous films with distinctive effective refractive indices, n_{eff} , of about 4 for the pure WS₂ 2D nanomesh,⁷⁴ and moving closer to 2 for the nanotube-rich sample where the cores of the nanotubes are air or WO_{3-x}.⁷⁵ In this approximation, the broad spectral features in the near-infrared region can be interpreted as antiresonances (manifested as dips in reflectivity) resulting

from interference of light reflected from the top and bottom interfaces of the effective WS₂ film, and the wavelength at which an antiresonance occurs increases with n_{eff} . In addition, the morphology of the film can affect how pronounced an antiresonance is: it is expected that the homogenous film approximation works better for the nanotube-rich sample than for the 2D nanomesh where the multiple 2D planes produce more scattering and higher overall reflectivity. Hence the antiresonance effect would manifest at larger wavelength and be weaker in the 2D nanomesh, which appears to agree with the experimental findings. More investigations are needed to clarify the origin of these broad spectral features.

Figure 7(d) presents spectral maps of the reflection intensity of each of the nanotube-rich and 2D nanomesh samples, as a function of the angle of incidence; measurements were taken with polarized light using the setup from Figure 7(c) (Methods). For both P-polarized light (upper panels) the spectral signatures appear to correlate well with those in Figure 7(b), including the A, B, and C features, and do not change significantly upon varying the angle of incidence. Consequently, these spectral signatures are specific to WS₂ as a material. For S-polarized light, the spectral maps are also modulated by the features shown in Figure 7(b), however there is a stronger contribution from the broad spectral features located above 700 nm. This suggests that the S-polarized light couples more effectively with the sample as a whole, hence these maps reflect more the geometric/morphologic characteristics of the two types of samples rather than being specific to their common WS₂ constituent material.

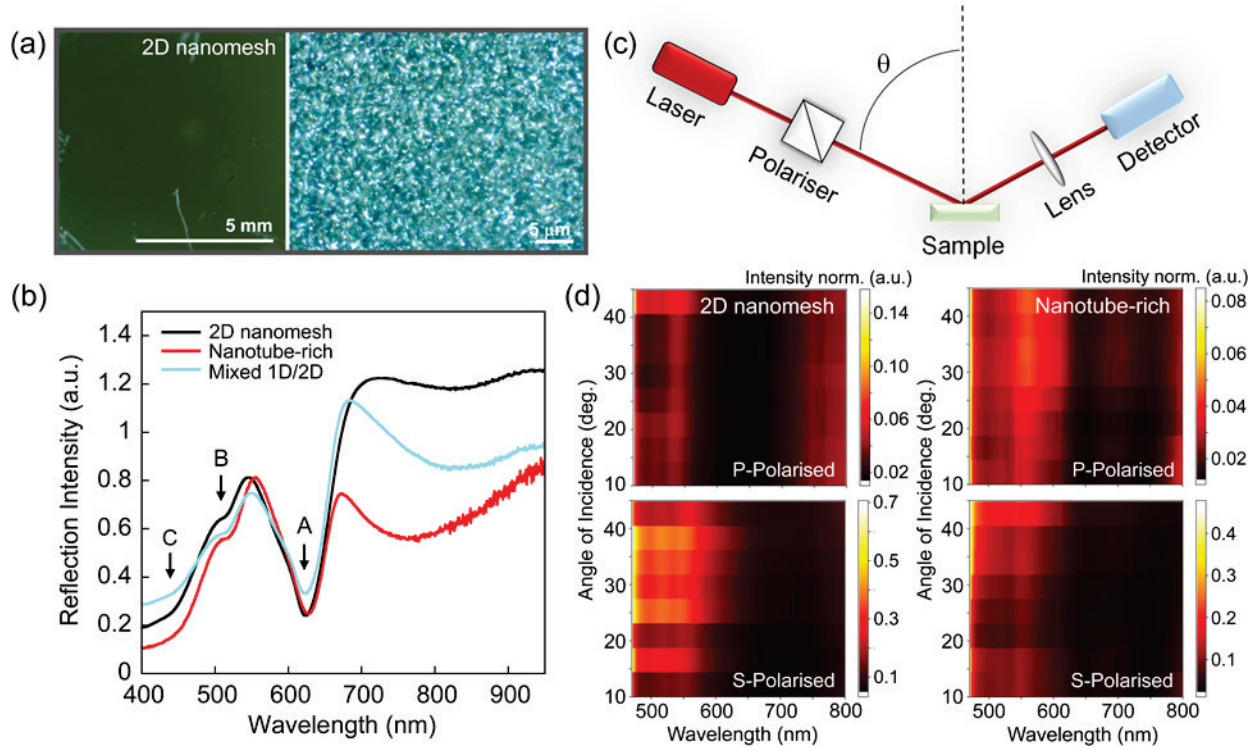


Figure 7. Linear optical properties of the class of out-of-plane WS₂ phases, showing representative phases: nanotube-rich (1D); intermediary, with mixed 1D/2D content; and 2D nanomesh. (a) Left, a photograph of the 2D nanomesh; right, a dark-field microscopy image from the 2D nanomesh, *via* a x100 objective. (b) Reflectivity spectra obtained in bright field microscopy at normal incidence with unpolarized light, from the three types of phases. (c) Experimental setup for the angular-dependent reflectivity measurements shown in (d). (d) Reflectivity spectral maps, as a function of angle of incidence, from the nanotube-rich (1D) and 2D nanomesh samples, and for P- and S-polarized light.

Because of their large second-order nonlinear susceptibility, 2D materials such as WS₂, are of significant interest for nonlinear optical devices.^{17,76-79} We measured the second harmonic generation (SHG) for the same three types of samples investigated in Figure 7(b), in the reflection geometry, using the setup from Figure 8(a). SHG is a nonlinear optical technique whereby two

photons at the fundamental frequency are annihilated to create a third photon, at double the frequency. Because this frequency-doubling process is exquisitely symmetry-sensitive, it is used to characterize symmetry breaking effects, such as externally applied electric⁸⁰ and magnetic⁸¹ fields, strain,⁸² chirality,⁸³ localized surface electric fields,⁸⁴ and surface roughness, down to the atomic monolayer.⁸⁵

The experiments were conducted using a fundamental (incident) light of 800 nm wavelength, and 100 fs laser pulses. Figure 8(b) shows the SHG intensity (at 400 nm) as a function of incident power of the fundamental light (at 800 nm), for the nanotube-based (1D-rich), intermediary with mixed 1D/2D content, and the 2D nanomesh samples, respectively. As a reference, the SHG signal generated by the Si substrate, which is a centrosymmetric material with low SHG response,^{86,87} is also shown. All three types of WS₂ samples are extremely non-linear, showing between 10⁴ to 10⁵ larger SHG intensity than Si at a given power. It should be noted that our SHG setup is built for sensitivity, with a detector upper limit set to about 10⁵ counts/s, which imposes an experimental limit on the power incident on the sample. Figure 8(b) also unambiguously shows the SHG response is influenced by the type of WS₂ phase making up the sample: it is lowest, though still sizeable, in the nanotube sample, increases for the sample with intermediary 1D/2D mixed content, and is largest in the 2D nanomesh. Indeed, the WS₂ 2D nanomesh has several symmetry-breaking attributes that favor SHG: (i) it is made of mono- to three-layer sheets, as confirmed by TEM images and location of excitonic features in the reflectivity spectra, (ii) has considerable roughness arising from the formation of 2D platelets spreading around the initial 1D skeleton (as depicted in Figure 4(a)), and finally (iii) WS₂, in particular, benefits from the strong electric dipole established in the unit cell and linked to strong spin-orbit interaction. It is known that SHG is strongly enhanced in transition metal dichalcogenides (TMDs) with odd number of layers where the unit

cell lacks inversion symmetry, and is strongest in the monolayer limit,⁸⁸ and for this reason, for non-linear optics applications, such materials are exfoliated by various methods in order to then create stacks of isolated sheets.^{16,76} In the case of our WS₂ 2D nanomesh, the material grows directly on the substrate as “exfoliated” sheets of mono- or low number of layers, and large quantities within a high-density film of several microns in thickness, hence favouring non-linear optical response.

Figure 8(b) also shows that, while the Si reference response follows the expected quadratic curve for the SHG power as a function of the fundamental excitation power,⁸⁹ this is not the case for the WS₂ samples. All three WS₂ samples (nanotubes, with mixed 1D/2D content, and 2D nanomesh) deviate from the quadratic dependence and the deviation is strongest for the 2D nanomesh. This can be observed visually, but is clearly reflected by the differing R^2 values of the fit curves (see caption of Figure 8(b)). This power-dependent divergence can be attributed to the onset of saturable absorption, which correlates with increasing presence of edge states⁹⁰ induced by the finite lateral sizes/domains of 2D nanosheets that form when the material progresses from 1D form to full 2D content.

The very large values of SHG and promising saturable absorption properties in these materials, in particular in the 2D nanomesh, together with the ability to be grown on insulating, transparent substrates (demonstrated here on SiO₂) point towards promising nonlinear optical applications, which will be the subject of future work.

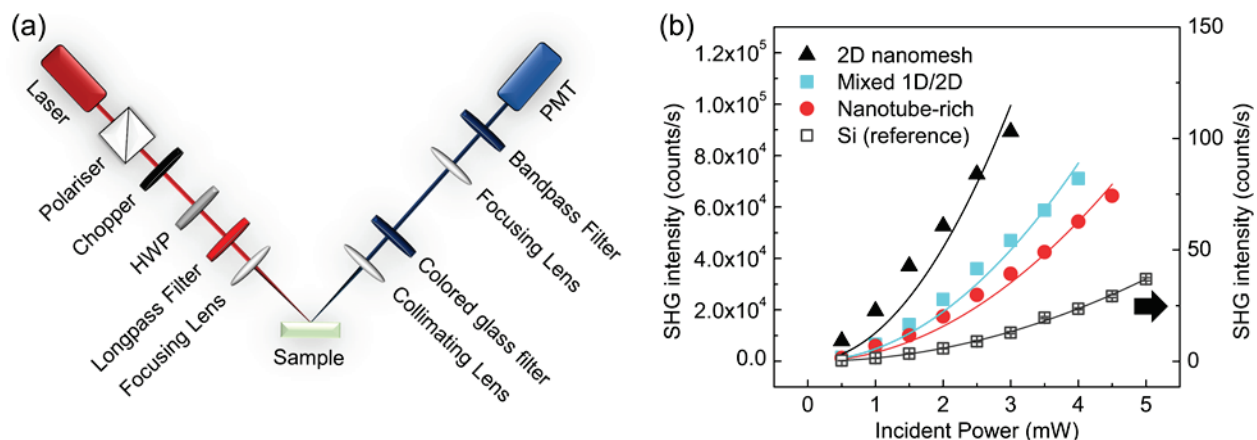


Figure 8. Nonlinear optical properties of the class of out-of-plane WS₂ phases, showing representative phases: nanotube-rich (1D); intermediary, with mixed 1D/2D content; and 2D nanomesh. (a) Experimental setup. HWP designates a half wave-plate and PMT stands for photo multiplier tube. (b) Second harmonic generation (SHG) intensity as a function of the incident power, for the three types of WS₂ samples (left Y axis) and for the Si substrate used as a reference (right Y axis, indicated by black arrow). Error bars representative for the experiment can be seen in the low signal data from Si; these are too small to be visible on the WS₂ data. The continuous lines are fits to quadratic functions characteristic of SHG behavior ($R^2 = 0.91$; 0.97 ; 0.98 ; and 0.998 for the 2D nanomesh, mixed 1D/2D content, nanotube-rich (1D) samples, and Si substrate, respectively); deviations of data from these lines demonstrate onset of saturable absorption.

Conclusions

In conclusion, we demonstrated the sequential growth by CVD of a wide range of nanostructured materials, ranging from 1D WO_{3-x} suboxides to WS₂ nanophases with tunable 1D to 2D content, by intentionally decoupling into two stages (first stage, partial reduction; second stage, sulfurization) a reaction from WO₃ to WS₂ in order to enhance and reveal the role played by W

suboxides in CVD growth of WS₂. In this process, we created WO_{2.92}/WO_{2.92} morphologies, such as nanowires and nanorods, grown in-plane (*i.e.* parallel to the substrate) or out-of-plane of the substrate; the stoichiometry of these suboxides being found instrumental in the subsequent creation of many WS₂ polymorphs. We were, thus, able to exploit a WO_{3-x} – intermediate route that is very versatile, in that it is able to create by relatively simple tuning of the CVD growth process, and in a single process stream, a rich variety of 2H-WS₂ phases: a tunable class of materials, ranging from nanotubes, to mixed 1D and 2D WS₂ phases, to an out-of-plane (of the substrate), pure WS₂ 2D nanomesh with extended 2D few-layer crystallites; as well as in-plane (parallel to the substrate), self-seeded 2D domains. Regarding the in-plane 2D WS₂ films, our study showed that their growth can be routed *via* WO_{3-x} suboxides, a different route than *via* W oxo-sulfides as previously demonstrated in conventional 2D growth. Moreover, their growth proceeds *via* a “self-seeding and feeding” mechanism from 1D WO_{2.92}/WO_{2.92} nanorod precursors which may be able to take advantage of the positional and orientational growth within the substrate that can be achieved in growth of such 1D precursors.

The CVD route enables the growth of microns-thick WO_{3-x} suboxide nanowire films and WS₂ phases with tunable 1D/2D content directly on substrates, in an evolutionary manner, and on areas of at least several cm² (limited here by the dimensions of our furnace). WO_{3-x} suboxide nanowire films can find their own applications as sensing materials. The morphological tunability of the WS₂ phases can be exploited to tune their opto-electronic properties. In the examples given here, the evolution from WS₂ nanotubes with WO_{3-x} cores into a pure WS₂ 2D nanomesh phase results in changes in the optical absorption/reflection spectra, and can provide media with tunable effective refractive index. All WS₂ nanophases in the class have very strong non-linear optical properties, with the 2D nanomesh being extremely SHG active. Films obtained by condensation

of TMD suspensions, or composites of nanoscale TMD flakes with polymers have been suggested in other works for non-linear optical applications. The 2D nanomesh demonstrated here, however, has a “ready-made” sheet-exfoliated morphology, large overall effective thickness of the film, and ability to be grown directly on optically compatible substrates (*i.e.* insulators and transparent, as opposed to metallic) which are all important advantages in terms of ease of coupling with optical systems and devices, as well as improved material stability.

Methods

Synthesis of nanophases and nanostructures. A home-built setup involving a horizontal furnace with a temperature gradient (Supporting Information, Figure S1) was used to first produce a variety of W suboxide nanowires/nanorods (by partially reducing WO_3 to suboxides) – stage 1; which were then sulfurized for conversion to WS_2 nanophases – stage 2.

Synthesis of W suboxide nanowires and nanorods (stage 1). This is a Low-pressure CVD (LPCVD) process. The geometrical configuration of the furnace and position of boats with precursor materials are shown in Supporting Information, Figure S1. Differences in process substrate position/temperature, discussed in the main text, led to the formation of (i) long, out-of-plane nanowires, (ii) clusters of short nanorods, and (iii) in-plane nanorods of suboxides, as described below.

WO_{3-x} nanowires/nanorods were synthesized on SiO_2/Si (*i.e.* 300 nm thermal oxide), without any catalysts. Typically, 60 mg tungsten (VI) oxide (99.998%, Alfa Aesar) and 400 mg sulfur powder (99.5%, Alfa Aesar) were used as precursors. The SiO_2/Si substrates were cleaned by sonication in acetone, isopropanol (both HPLC grade), and deionized water, in sequence, prior to loading them in the furnace. A rotary pump pumped the tube during the whole process. Only argon (flow rate 150 sccm) was used for transporting the WO_3 and sulfur vapor to the Si/SiO_2 substrates. This LPCVD stage has two distinct periods: (i) an initial period where just WO_3 is sublimed (without S vapor being introduced into the reactor), a set of typical conditions being 1030 °C, at a pressure below 10^{-1} mBar, and for 20 minutes; followed by (ii) a period where S is introduced and co-evaporated together with the WO_3 over 15 minutes, leading to partial reduction of the WO_3 vapor, and, then, its condensation on the substrate as $\text{WO}_{2.92}$ and $\text{WO}_{2.9}$ nanostructures.

We have verified in dedicated experiments that in the conditions described at (i) WO_3 is volatile during our LPCVD process: after annealing (non-hydrated) WO_3 powder for 45 minutes, its weight decreased by two thirds, while the remaining powder in the furnace pocket was verified by XRD to still be entirely WO_3 (*i.e.* did not undergo any unexpected reduction) at the end of the annealing period. No nanowires were formed on the SiO_2/Si substrates after just this process.

Synthesis of out-of-plane WS_2 nanotubes, mixed 1D and 2D phases, and 2D nanomesh (stage 2). This is an Atmospheric pressure CVD (APCVD) process. Out-of-plane $\text{WO}_{2.92}/\text{WO}_{2.9}$ nanowires on SiO_2/Si were heated in the 850 - 925 °C range, under atmospheric pressure in the furnace center, whereas 400 mg sulfur powder (99.5%, Alfa Aesar) was heated upstream (about 40 cm) at 180 °C. Argon, at a flow rate of 100 sccm, was used to transport the sulfur vapor to the nanowires on SiO_2/Si sample. The same furnace geometry as above was employed. For generating Figure 4, where the transition between nanotube and 2D nanomesh phases was monitored, identical parts of the same initial $\text{WO}_{2.92}/\text{WO}_{2.9}$ nanowire sample were reacted at 850 °C in S environment (in the conditions described above), each for an increasing amount of time (Δt) up to three hours, to form the series described in the figure caption.

We have also verified (by a combination of SEM, TEM and XRD) that $\text{WO}_{2.9}$ and $\text{WO}_{2.92}$ are non-volatile in the conditions of our APCVD process by annealing the $\text{WO}_{2.92}/\text{WO}_{2.9}$ nanowires (supported by their SiO_2/Si substrate) for one hour just in an Ar atmosphere (*i.e.* without the presence of S) in APCVD conditions, and over the same temperature range at which the various WS_2 phases were obtained (as described above).

Synthesis of in-plane, 2D WS_2 domains (stage 2). As-grown $\text{WO}_{2.92}/\text{WO}_{2.9}$ short nanorods on SiO_2/Si were heated in the 850 - 925 °C range in the center of the furnace, under atmospheric pressure (*i.e.* in an APCVD process), while 400 mg sulfur powder (99.5%, Alfa Aesar) was heated

upstream (about 40 cm) at 180 °C. Argon, at 100 sccm flow rate, was used to transport the sulfur vapor to the nanorods on SiO₂/Si sample. The same furnace geometry as above was employed.

Structural characterization of grown nanophases and nanostructures.

X-ray diffraction (XRD). WO_{3-x} nanowires/nanorods and WS₂ nanomesh as grown on their SiO₂/Si substrates were characterized by XRD performed on a BRUKER AXS D8 Advance instrument, equipped with a Vantec-1 detector, and using CuK α radiation at $\lambda = 1.5418$ Å.

High resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED). Complementary HRTEM and SAED were performed on a JEOL JEM-2100Plus microscope operated at 200 kV and using a bottom-mounted CCD camera. A drop of nanowires/nanotubes/nanomesh suspension in ethanol was drop-cast onto a mesh TEM support grid.

Raman spectroscopy. All nanostructures, as grown on their SiO₂/Si substrates – WO_{3-x} nanowires/nanorods, WS₂ nanomesh, and in-plane, WS₂ 2D domains – were characterized by Raman spectroscopy performed with a Renishaw inVia Raman microscope, using 532 nm excitation laser. Samples were illuminated through a $\times 50$ objective lens (1.9 μm diameter spot size), at a laser power of 0.7 mW, while spectra were acquired with an exposure time of 1 s and using 200 accumulations.

Scanning electron microscopy (SEM). The nanostructured samples, as grown on the SiO₂/Si substrates, were observed using a JEOL SEM6480LV microscope in secondary electrons (SE) mode with acceleration voltages in the 5-15 kV range depending on the penetration depth needed for the various morphologies.

Linear and non-linear optical properties.

Microscopy and normal incidence reflection measurements. An Axioplan 2 microscope (ZEISS) with a halogen lamp and a 100x microscope objective were used, measurements being performed in brightfield mode. Microscope colour images were taken with an AxioCam 105 color camera, while optical spectra were taken over the 400 – 950 nm spectral range with an Ocean Optics QE Pro spectrometer, using an integration time of 1 s and averaging over 10 scans. The spectra were normalized with respect to the untreated silicon wafer.

Angle-dependent linear optical characterization. A Fianium SC400-2 2 W laser source with a 1064 nm output wavelength and 20 MHz repetition rate and a 5 ps pulse spliced to an in-house fabricated supercontinuum fibre⁹¹ capable of a 450-2400 nm spectral range was used. Two uncoated Glan-Laser polarizers were used to control the power output and polarization of the incident light. The reflected light from the sample was collected *via* a 200 μ m diameter SMA fibre (0.22 NA) mounted on a fibre launch stage and measured with an Ocean Optics QE Pro spectrometer over 450 – 950 nm, using an integration time of 300 ms and averaging over 10 scans. An automated setup was used to determine the reflected light angle. The spectra were normalized with respect to the untreated silicon wafer.

Second harmonic generation (SHG) measurements. A femtosecond laser (MaiTai HP from Spectra Physics), tuned to a wavelength of 800 nm, provided the incident fundamental beam. The laser produced pulses at a repetition rate of 80 MHz, which are approximately 100 fs long in time with a bandwidth of 10 nm. Two crossed polarizers (Glan-laser calcite anti-reflection coated) controlled the laser power. An achromatic half-waveplate ensured that the incident beam is P-polarized (horizontal polarization). Two colored glass bandpass filters were used to reject any spurious light at the second harmonic. An achromatic lens (focal length 150 mm, anti-reflection coated) focused the beam onto the sample at an incident angle of 45° relative to the sample.

Another achromatic lens (focal length 150 mm, anti-reflection coated) collimated the SHG in reflection, while a colored bandpass filter rejected the fundamental beam, leaving only the SHG. The signal beam was focused into a cooled photomultiplier tube (PMT) using an anti-reflection coated lens (focal length 200 mm). The PMT produced current pulses, which were pre-amplified and fed into a gated photon counter. The data point for each incident power was the average of 20 measurements, where the counting duration of each measurement was 5 seconds.

Supporting Information

(i) CVD setup for nanostructure synthesis, and phase diagram for WO_{3-x} phases. (ii) Characterization (XRD, SEM and HRTEM) of grown WO_{3-x} nanowires and nanorods. (iii) Raman characterization of WS_2 nanophases. (iv) Electrical characterization of WS_2 2D nanomesh. (v) Atomistic description of layer-by-layer evolution from WO_3 to WS_2 *via* $\text{WO}_{2.92}/\text{WO}_{2.9}$ Magnéli phases.

Author Contributions

AI and ZL designed the material growth-related program of work, while AI supervised the work; ZL performed the experiments; ZL and AI analyzed the data and co-wrote the growth part of the paper. VKV and AI selected the optical measurements performed. VKV supervised the optics-related work. AWAM, CK, DCH performed the optics experiments; together with VKV and AI (with contributions from ZL), they analyzed the data and co-wrote the optics-related part of manuscript.

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